SYNTHESIS AND CHARACTERIZATION OF HYDROXYAPATITE

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology
in
Ceramic Engineering

By
PREETAM JENA

Department of Ceramic Engineering
National Institute of Technology
Rourkela
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Under the Guidance of
Dr. SUKUMAR ADAK

Department of Ceramic Engineering
National Institute of Technology
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2007

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Rourkela

CERTIFICATE

This is to certify that the thesis entitled, "SYNTHESIS AND CHARACTERIZATION OF HYDROXYAPATITE" submitted by Sri Preetam Jena in partial fulfillments for the requirements for the award of Bachelor of Technology Degree in Ceramic Engineering at National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

Date:

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Dept. of Ceramic Engineering
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30th April 2007 **PREETAM JENA**

CONTENTS

ABSTRACT

The current work deals with the synthesis and the subsequent characterization of HAP. The characterization involves analysis of X-ray diffraction, Scanning Electron Microscope, Particle size measurement, Thermogravimetric Analysis (TGA), Sintering and Pressing.

In my project I have prepared HAP by the *chemical precipitation method.*. There was also an experiment undertaken in order to ascertain if there is any change in pH by changing the stages of pH correction XRD patterns were studied of calcined and pre calcined HAP powders. Then the HAP produced was divided into 36 diff 0.8 g batches which were sintered in 3 batches at 1000^0C, 1100^0C & 1200^0C amd then their respective densities were studied.

From all the studies made we found out that there is an improvement in crystallinity of HA after calcination. Thermal stability is only upto 1300C.

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Chapter 1

GENERAL INTRODUCTION

1.1 INTRODUCTION

Hydroxylapatite, also frequently called hydroxyapatite, is a mineral. It is a naturally occurring form of calcium apatite with the formula Ca5(PO4)3(OH), but is usually written Ca10(PO4)6(OH)2 to denote that the crystal unit cell comprises two molecules. Hydroxylapatite is the hydroxyl end member of the complex apatite group. The OH- ion can be replaced by fluoride, chloride or carbonate. It crystallizes in the hexagonal crystal system. It has a specific gravity of 3.08 and is 5 on the Mohs hardness scale. Pure hydroxylapatite powder is white. Naturally occurring apatites can however also have brown, yellow or green colorations. Compare to the discolorations of dental fluorosis.

1.2 RELEVANCE IN MEDICAL FIELD

Hydroxylapatite is the main mineral component of bone. Carbonated-calcium deficient hydroxyapatite is the main mineral of which dental enamel and dentin are comprised.Consequently HA was readily considered as a bioactive material for artificial bone substitution because of its biocompatibility, and chemical and biological affinity with bony tissue.Known that the optimum Ca/P molar ratio must be 1.667, HA with approximately this ratio is easily produced from water systems both by precipitation and by hydrolysis, with temperature ranging from 20 to 95*C and with pH values ranging from 6 to 8.

1.3 FACTS AND FIGURES

- **Chemical Formula:** $Ca_5(PO_4)_3(OH)$
- **Composition:** Molecular Weight = 502.31 gm

Calcium	39.89 %	Ca	55.82 % CaO
Phosphorus	18.50 %	P	42.39 % P_2O_5
Hydrogen	0.20 %	H	1.79 % H_2O
Oxygen	41.41 %	O	
	100.00 %		100.00 % = TOTAL OXIDE

- **Empirical Formula:** $Ca_5(PO_4)_3(OH)$
- **Name Origin:** Named as the hydroxyl end-member and from the Greek apatao - "I am misleading."
- **Synonym:** Apatite
  Deltaite-mixture with crandellite
  Hydroxy Apatite
  ICSD 203027
  PDF 9-432

Physical Properties of Hydroxylapatite

- **Cleavage:** [???] Indistinct
- **Color:** Colorless, White, Gray, Yellow, Yellowish green.
- **Density:** 3.08
- **Diaphaniety:** Transparent to Opaque
- **Habit:** Massive - Granular - Common texture observed in granite and other igneous rock.
- **Hardness:** 5 - Apatite
- **Luster:** Vitreous - Dull
- **Streak:** white

Optical Properties of Hydroxylapatite

- **Gladstone-Dale:**

CI= -0.046 (Good) –
where the CI = (1-KPDmeas/KC)
CI calc= -0.02 (Excellent)
where the CI = (1-KPDcalc/KC)
KPDcalc= 0.2049,KPDmeas= 0.2102,KC= 0.2009

- **Optical Data:**

Uniaxial (-), e=1.644, w=1.651, bi=0.0070.

1.4 SUPERIORITY OVER COMPATRIOTS

☞ *Metals*: It reacts at body temp(37OC) and pH(7.4)when kept for many years.

☞ *Inert Materials:* A fibrous tissue of variable thickness is formed which leads to tumor.

☞ *Reabsorbable Material*: It dissolves at a faster rate than its replacement by the surrounding tissues.

1.5 USES IN DIFFERENT FORM

- Ceramics used in health care industry in the past
  - Eye Glasses
  - Diagnostic instruments
  - Chemical Ware
  - Fibre Optics for Endoscopy
  - Thermometer
  - Tissue culture flasks
  - Carriers for Enzymes and antibodies etc.

- Recent Uses
  - Replacement for the inorganic component of bones and teeth
  - Dental and orthopedic implant
  - HAP coated material

1.6 ORGANIZATION OF PROJECT REPORT

Preliminary introduction about HAP with different characters, chemistry, application and relevance of HAP and organization of project report is discussed in chapter 1. Chapter 2 provides a detailed discussion of literature on the various methods of preparation of HAP under different circumstances is mentioned. The main objective of the present work, which is based on the literature survey, is presented towards the end of chapter 2. In chapter 3, the various synthesis and characterization techniques used in the present work are described in detail. Chapter 4 describes the results of HAP characterization. The synthesis and characterization of HAP prepared through chemical precipitation using (NH4)2HPO4, $Ca(NO_3)_2$ & $Ca(NO_3)_2.4H_2O$.Finally, conclusions of project work are given in Chapter 5.

Chapter 2

LITERATURE REVIEW

.1 PREAPARATION TECHNIQUES

2.1.1 First precipitation process

They employed calcium and phosphorus precursors in solutions.The experimental development involved the addition of 100 mL of a solution of 0.6 M of phosphoric acid(H3PO4) (Merck, 85%) to 100 mL of a suspension of 1.0 M calcium hydroxide (Ca(OH)2) (J.T.Baker, 97%) at a speed of 7 mL/min. The chemical equation that describes he reaction is:

- $10Ca(OH)_2 + 6H_3PO4 \longrightarrow Ca_{10}(PO_4)_6(OH)_2 + {}_{18H2O}$ (1)

Figure 1 shows the first experimental precipitation process.A digital potentiometer Orion Mod. 1520 was used to measure the pH of the solution during mixing and aging. The mixture was warmed to 90±C for 1 hour to activate the chemical reaction and then stirred for another hour. During aging at room temperature, the HA was precipitated, filtered and washed with distilled water. The dried powder was calcined at up to 850±C for 4 to 6 hours; the obtained product was crystalline.

2.1.2 Second precipitation process

The method was described by Hayeck and Stadlman. The starting reagents were tetrahydrated calcium nitrate (J.T.Baker, 99,9%), phosphate monoacid of diamino (J.T. Baker, 98,5%) and ammonium hydroxide (J.T.Baker 20-30%). In an Erlenmeyer flask containing 300 mL of 1 M of $Ca(NO_3)_2\ 4H_2O$ solution, 200 mL of 0.6 M of $(NH_4)_2HPO_4$ solution was added at a rate of 22 mL/min, and 14 mL of NH_4OH, maintaining the system at 95±C with constant stirring for one hour, (Fig. 2).The equation of the chemical reaction is:

- $10({}_{CaNO3})2{:}4H2O + 6(NH_4)_2HPO_4 + 8NH_4OH$

$$\longrightarrow Ca_{10}(PO_4)6(OH)2 + 20NH_4NO_3 + 46H_2O$$

The mixture was aged for 14 days at room temperature.After this period, the obtained precipitate was filtered and washed several times with distilled water. Then it was dried at 250±C for 3 hours and calcined at 850±C.

2.1.3 Sol-gel (PSG) Process

Triethyl phosphate (Aldrich, 99.8%) and calcium nitrate tetrahydrated (Baker, 99.9%) were used, as well as 2-metoxiethanol ether (Aldrich, 99.3%) as an organic solvent.Esther phosphate was hydrolyzed with the release of water during the first stage of the reaction, generating HA (18).The equation of the chemical reaction is:

- $10Ca(NO_3)24H_2O + 6(C_2H_5O)3P(O)+20CH_3O(CH_2)_2OH \longrightarrow Ca_{10}(PO_4)6(OH)2 + \text{subproducts}$ (3)

In order to obtain a Ca/P ratio of 1.667, 23.483g of $Ca(NO_3)24H_2O$, 10.2 mL of $(C_2H_5O)_3P(O)$ and 15.6 mL of $CH_3O(CH_2)_2OH$ were used. The container was closed and constantly stirred until a homogenous mixture was obtained.Figure 3 shows the procedure. Calcium nitrate tetrahydrated crystals and 2-metoxietanol were placed in a closed Erlenmeyer flask, stirring, and then triethyl phosphate was added. The mixture was aged for 4 days at 80±C with stirring.To start the gelation process the flask was opened andthe temperature increased to 90±C < T < 100±C. At the end of this stage there was a very viscous yellowish gel, which that was dried to obtain a grayish product and then washed.Finally it was calcined for 12h at 1200±C and HA was obtained.

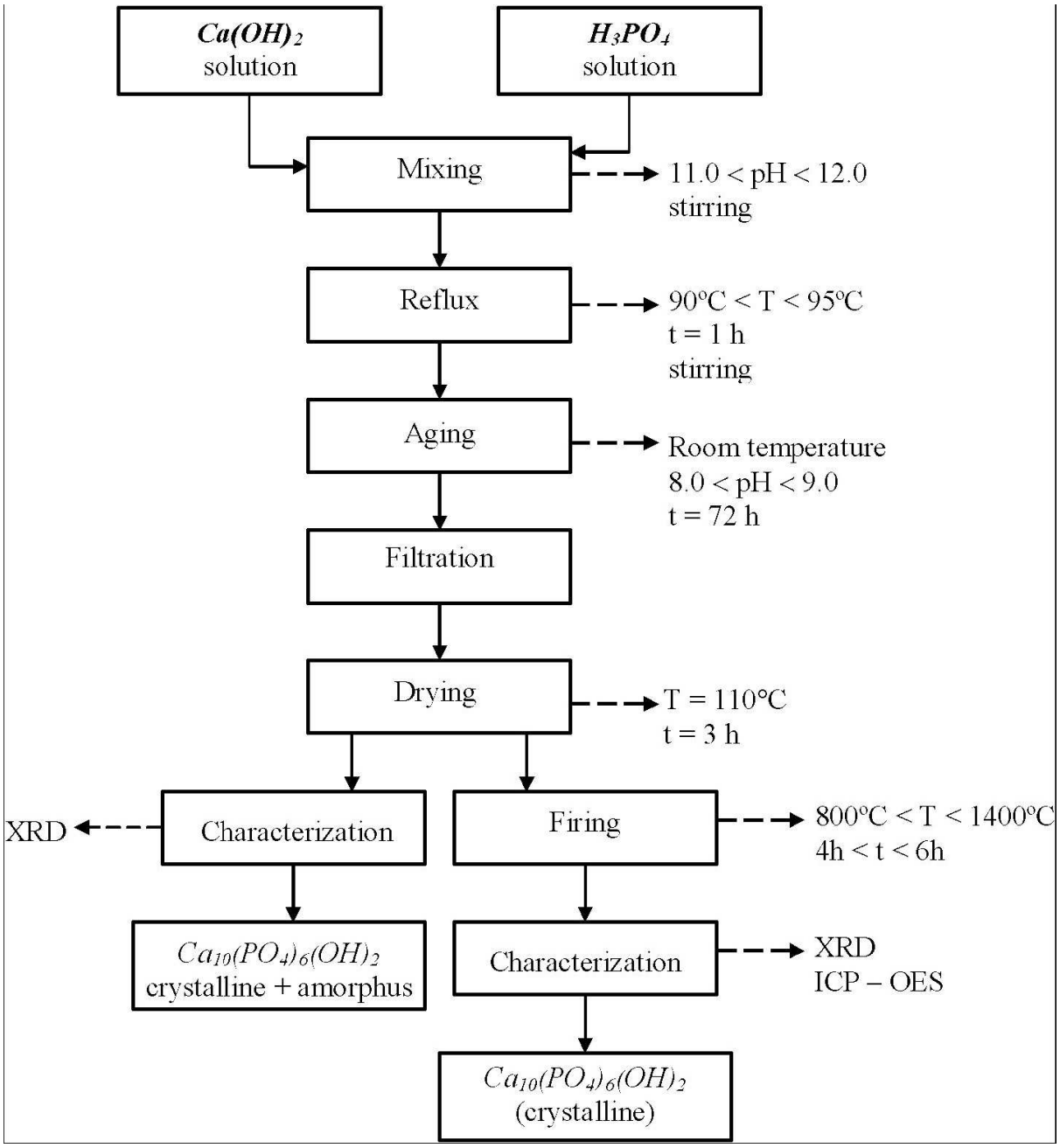

Fig. 1 Flow chart for the synthesis of HA by a second precipitation process.

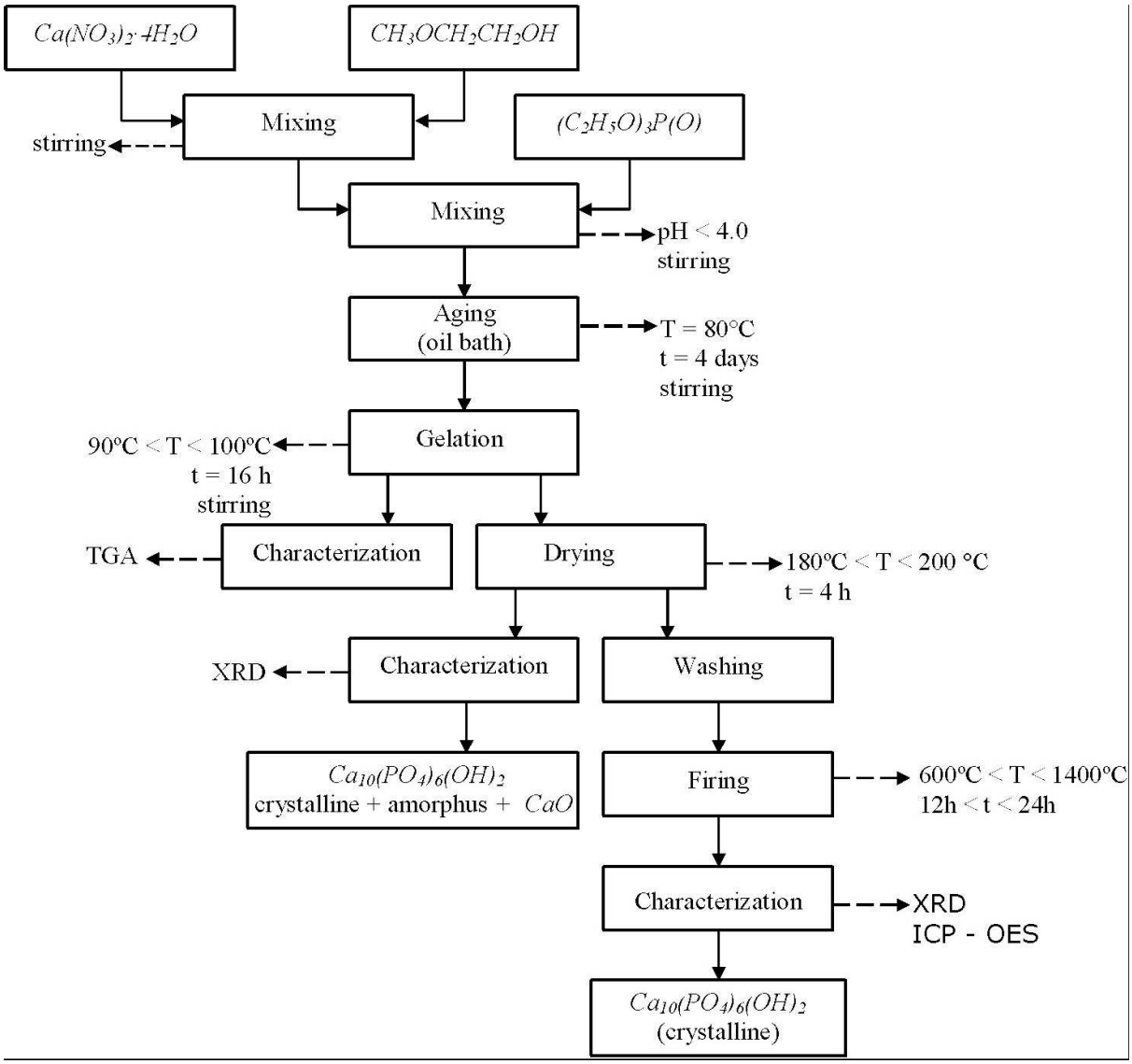

Fig 2 Flow chart for the synthesis of HA by a second precipitation process.

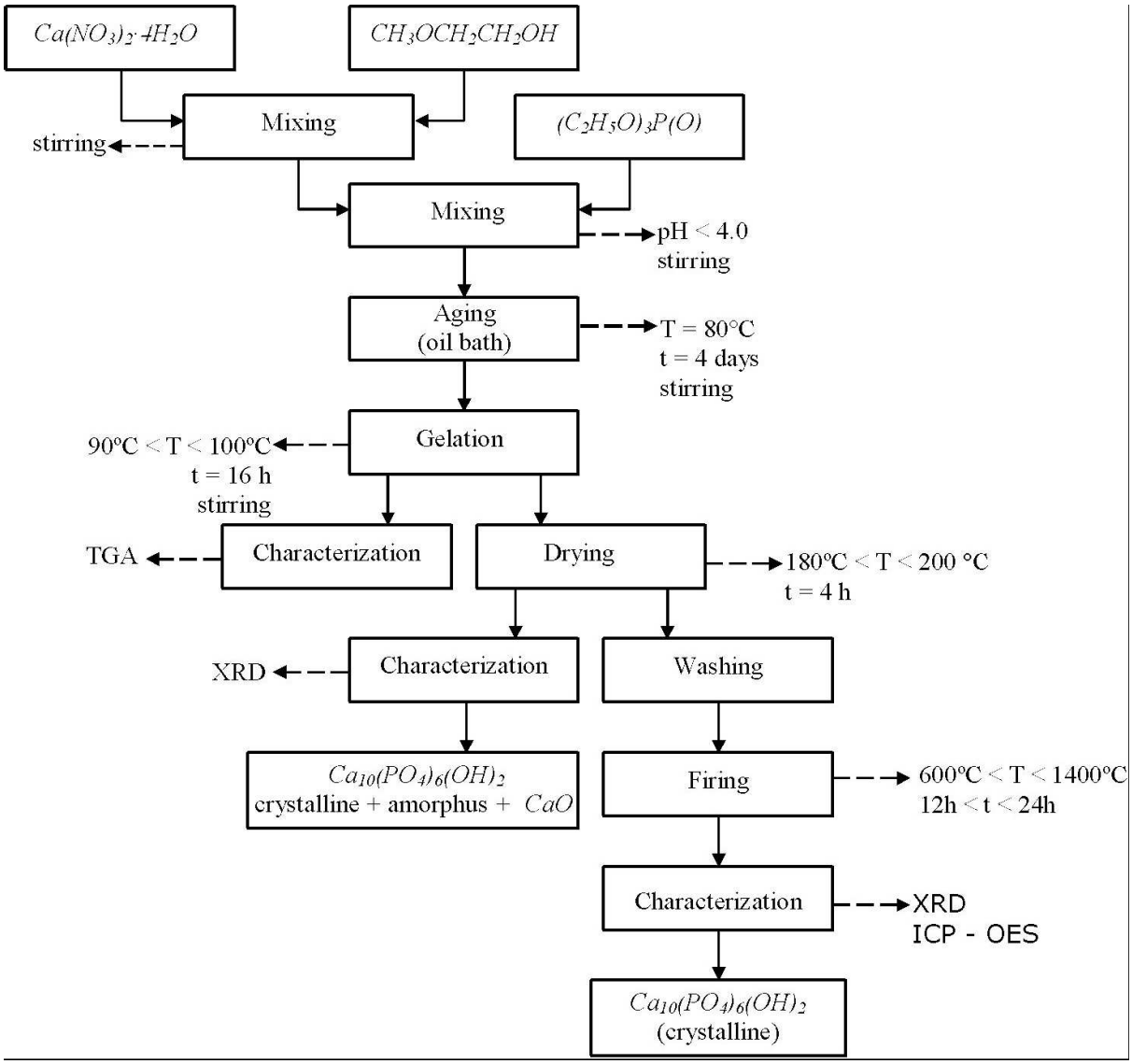

Fig. 3 Stoichiometric Hydroxyapatite obtained by ppt. & sol gel process

2.2 CHOICE OF THE BEST METHOD

Although the precipitation processes to obtain HA depend on variables such as pH, time of aging, temperature, etc., they are more effective and less expensive than the sol-gel process;
crystalline HA is obtained and the yield is better compared to the sol-gel process. The first precipitation process produces a more crystalline HA than the second process.
HAs obtained by precipitation processes are nonstoichiometric, with a Ca/P ratio < 1.67, whereas the one obtained by the sol-gel process is stoichiometric. Concentrations of
Pb, Cd, As and Hg are lower than those stipulated for medical applications. The HA obtained by the sol-gel process has a very high level for purity, a homogenous composition and
smaller cluster size. We conclude that each of the processes for obtaining HA
has its favorable qualities, and therefore it is important to choose the best one depending on the application.

2.3 SINTERING BEHAVIOUR OF HAP

The sintering behavior of HAP powders with different characteristics, allows the identification of deferent factors effecting sintering behavior and density of the final ceramics.At the beginning of the sintering, below 1000 ◦C, particle coalescence occurs without densification or with little densification. The particle coalescence usually associated with a reduction of the specific surface area [36]. The temperature, at which start of this coalescence occurs, decreases as the Ca/P ratio of the powder decreases.

Chapter 3

EXPERIMENTAL WORK

3.1 INTRODUCTION

Chemical precipitation technique is one of the important techniques for synthesizing HAP powder. In this work, HAP has been prepared by chemical precipitation techniques. Several different characterization techniques have been used to study the properties of HAP powders. In this chapter, the synthesis and characterization techniques are described in detail.

3.2 SYNTHESIS

The containers required to prepare the solution were washed properly with distilled water to avoid any kind of contamination.

A clear solution of $Ca(NO_3)_2$ for 10 g batch of HAP was prepared by adding 23.5g of $Ca(NO_3)_2 4H_2O$ in 60ml water followed by vigoeroes mixing for 1-2 mins with a magnetic stirrer, shich gives a clear solution of $Ca(NO_{32}$.

Then 7.88s of $NH_4.2HPO_4$ was added to the prepared solution to obtain a milky solution followed by vigorously mixing for 3-4mins. Then the prepared solution was heated upto 80C max. to the prepared solution required amount of concentrated ammonium solution was added with simultaneous rapid stirring with the help of a magnetic stirrer till the pH of the solution became greater than 10.

The white ppt. obtained was aged for 24hrs. at room temperature. The obtained powder was filtered out carefully using a filter paper and dried at 65C for 20 hrs in an oven.

3.3 CHEMISTRY

$$10\ Ca(OH)_2 + 6\ H_3PO_4 \longrightarrow Ca_{10}(PO_4)_6(OH)_2 + 18H_2O$$

Preparation of 10g batch of heydroxylapatite HAP by first method;

$$10Ca(NO_3)_2 + 6\ (NH_4)2HPO_4 + 2H_2O \longrightarrow Ca_{10}(PO_4)6(OH)_2 + 12\ NH_4NO_3 + 8\ HNO_3$$

For a batch of 50g of HAP we need;

- Amount of $(NH_4)2HPO_4$ used was 39.40g.
- Amount of $Ca(NO_3)_2$ used was 81.6730 g.
- Amount of $Ca(NO_3)_2.4H_2O$ used was 117.50g.

3.3 General characterization

3.3.1 Thermal properties

Thermal decomposition was studied using thermogravimetric and differential scanning calorimetric (TG-DSC) by heating the sample at 10 °C/min in argon in a thermal analyzer (Model STA 4096, NETZSCH , Germany)

3.3.2 X-ray diffraction

Phase analysis was studied using the room temperature powder X-ray diffraction with filtered 0.154056 nm Cu Kα radiation. Samples are scanned in a continuous mode from 25° – 90° with a scanning rate of 0.02 (degree) / 1 (sec).

3.3.3 Scanning Electron Microscope

Microstructural features were studied using Scanning Electron Microscope). For preparation of SEM sample, the powder is dispersed in isopropyl alcohol in an ultra sonication bath (20 kHz, 500 W) for half an hour. One drop of the welldispersed sample solution is deposited on to polished brass plate. This brass plate was used for microscopy.

3.4.5 Thermogravimetric Analysis (TGA)

The gel produced by the sol-gel process was studied by TGA to determine the mass variation in the sample. The sublimation temperatures of volatile substances were determined by DTA. The temperature interval was 1000±C ¸the heating rate was 5±C/min under nitrogen flow.

3.4.6 Pressing

The powder was divided into 36 ,0.8g packs n were pressed into pellets of approx. 12 mm diameter in uniaxial pressing machine at an optimum load 5000lb.

Chapter 4

RESULTS AND DISCUSSION

4.1 INTRODUCTION

This chapter describes the thermal behavior, structure, microstructure, density and IR spectroscopy of HAPpowder prepared through chemical precipitation technique using $(NH_4)2HPO_4$,$Ca(NO_3)2$ & $Ca(NO_3)_2.4H_2O$

4.2 RESULTS AND DISCUSSION

4.2.1 XRD patterns

Particle size in agglomerated or aggregated systems like hydroxyapatite powders is one of the most important parameters controlling ceramic processing. In this study, particle size of the powders were investigated using XRD (Scherrer equation) and laser diffraction. Each method of measurement senses a particular aspect of particle size. The profile broadening by powder X-ray diffraction senses monocrystalline domains. Laser diffraction method determines only the agglomerated. The HAP sample has a clear bimodal particle size distribution.

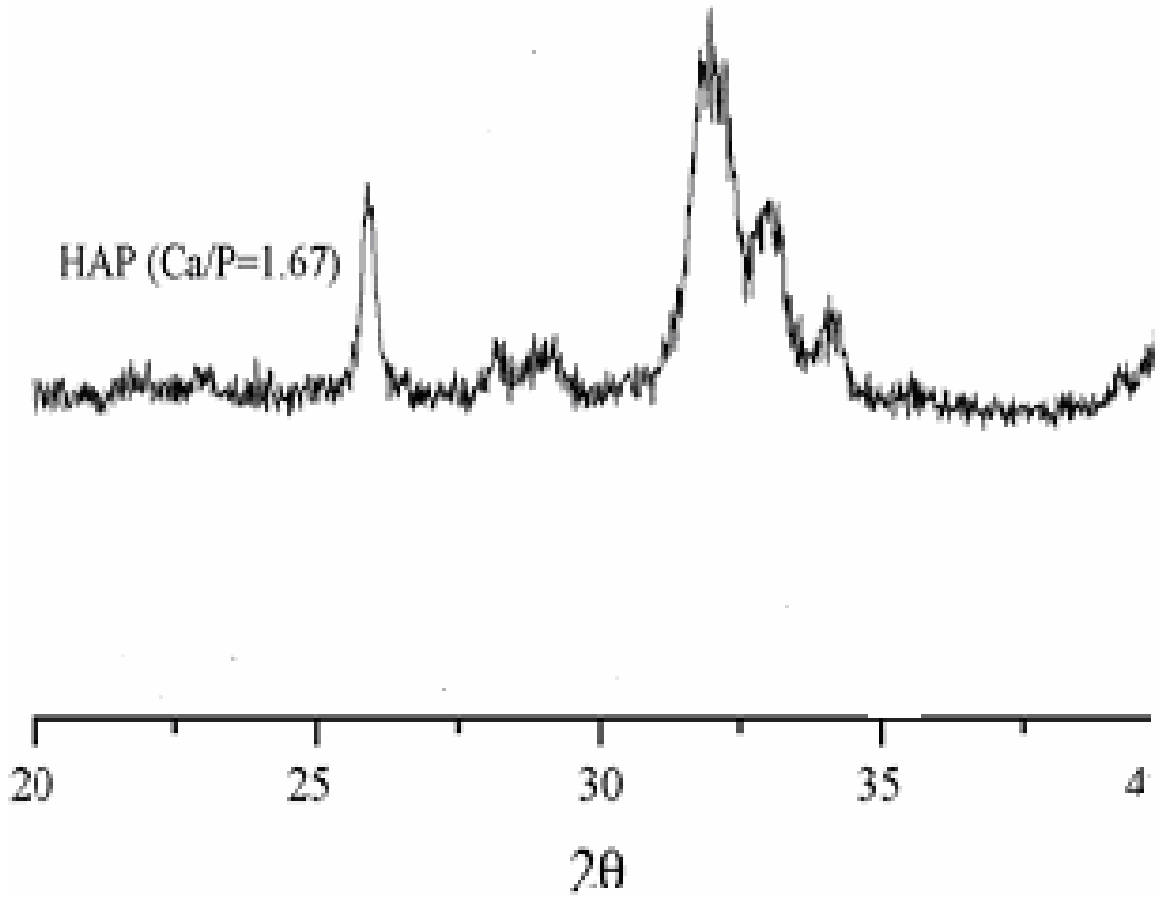

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Fig. 4. XRD patterns of hydroxyapatite powders dried at 100 ◦C for 24 h.

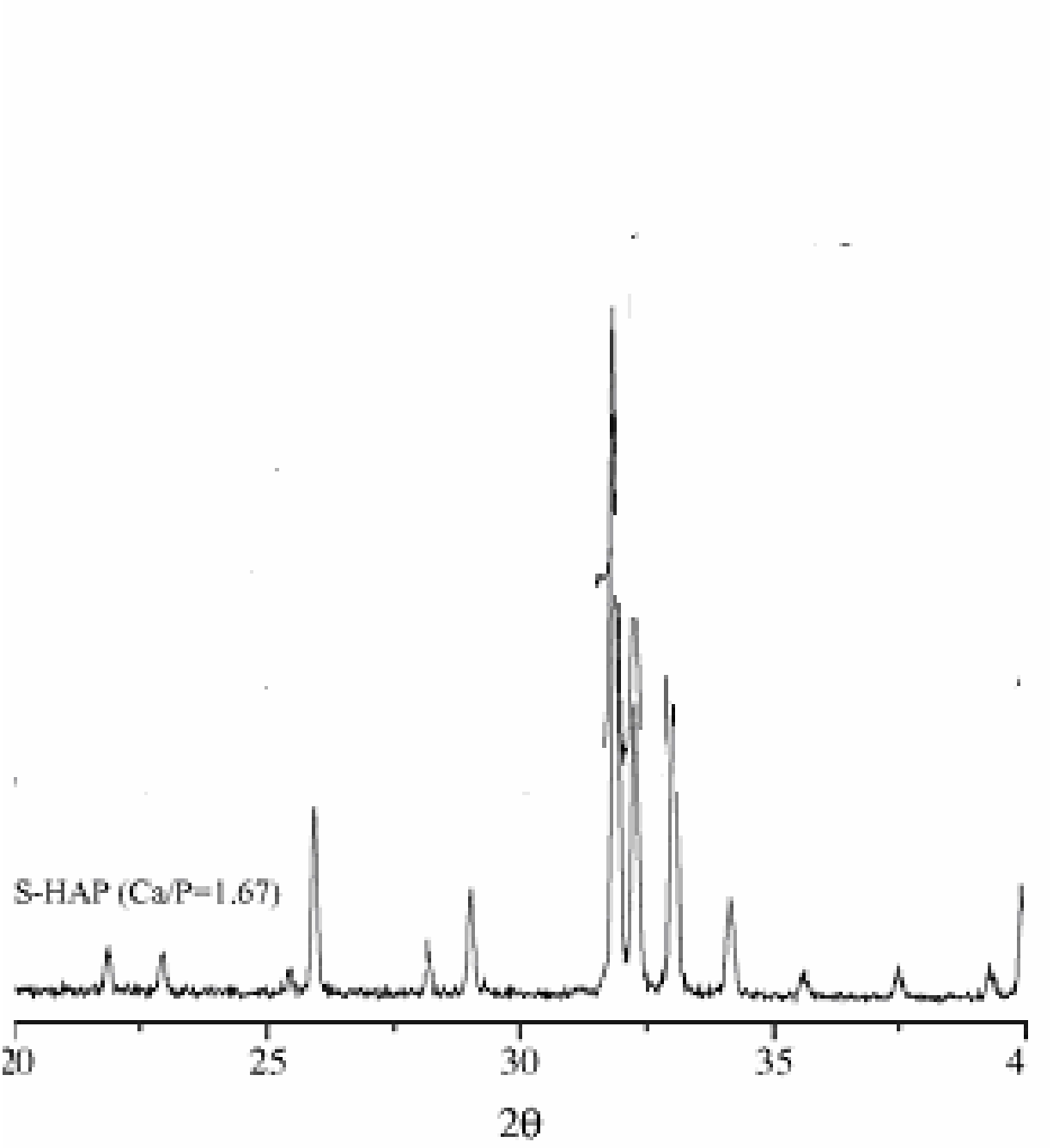


Fig. 5. ***XRD patterns of hydroxyapatite powders compacts sintered at 1100 ◦C.***

4.2.3 PARTICLE SIZE DISTRIBUTION

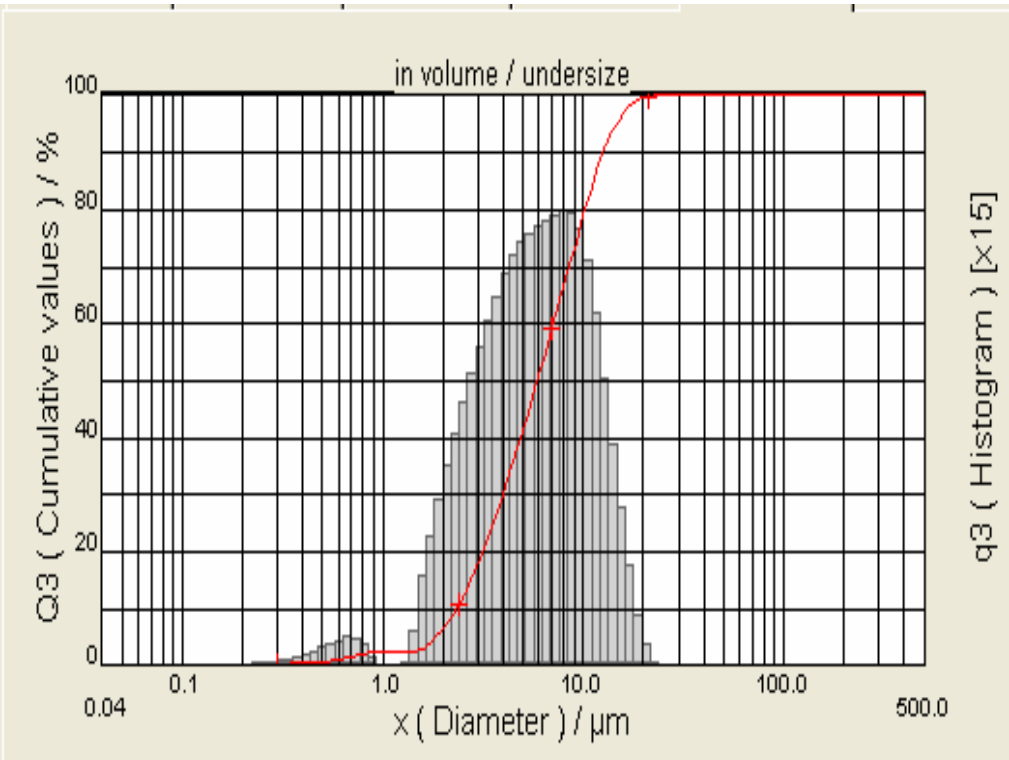


FIG.6.1 Particle size distribution of HAP uncalcined

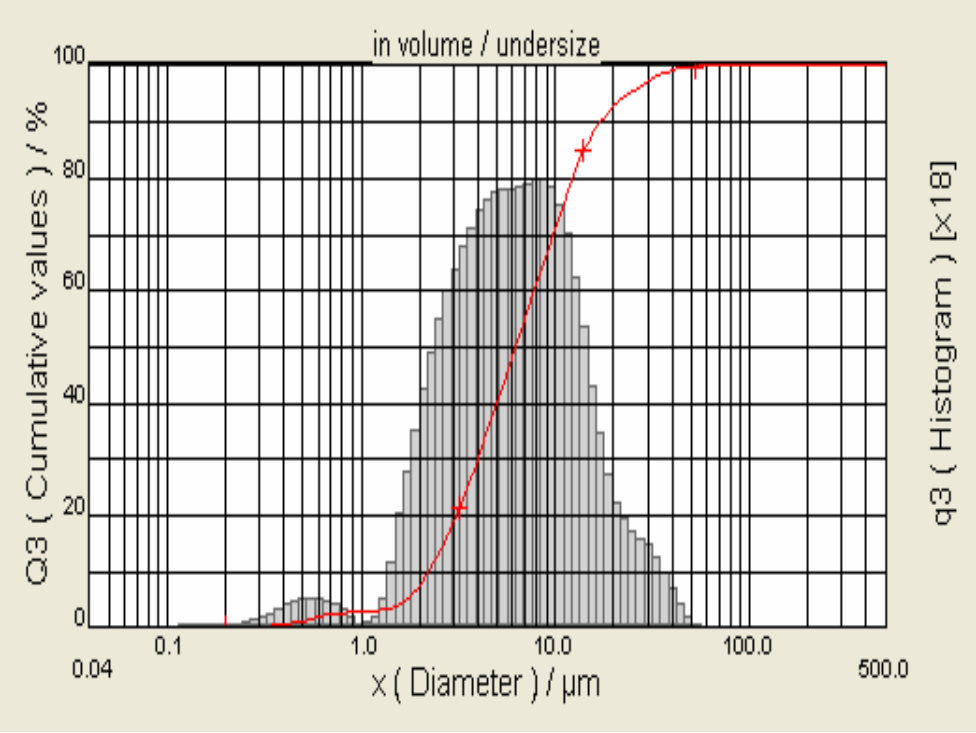
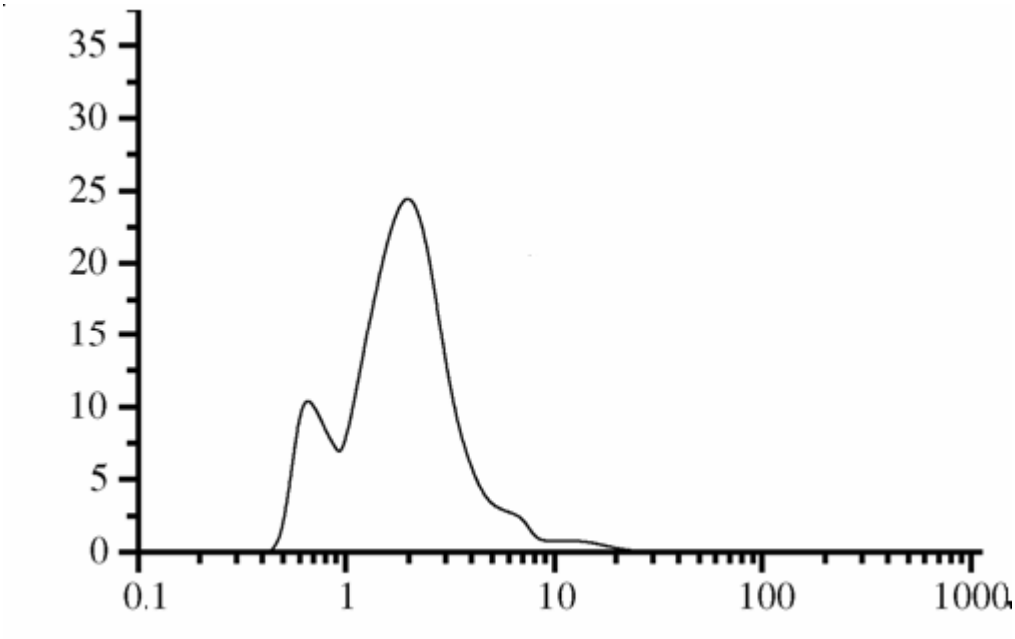


FIG6.2 Particle size distribution of HAP calcined at 1000C

The presence of two particle size ranges in case of HAP powders possibly reflects the aggregation in the submicrometer sizes range, yielding the so-called primary agglomerates (the first peak). These agglomerates continue to aggregate by forming interparticle bonds until they reach the micrometer size range, the second peak (>1 _m).



4.2.4 PRESSING

The powder was divided into 36 ,0.8g packs n were pressed into pellets of approx. 12 mm diameter in uniaxial pressing machine at an optimum load 5000lb.

Sample No.	Diameter (cm)	Thickness (cm)	Area (cm2)	Volume (cm3)	Weight (gms)	Density (gm/cc)
1	1.024	0.218	.8235	.1795	.3532	1.96
2	1.024	0.180	.8235	.1482	.3020	2.03
3	1.020	0.138	.8171	.1128	.2250	1.99
4	1.022	0.138	.8203	.1132	.2213	1.95
5	1.022	0.150	.8203	.1230	.2542	2.06
6	1.026	0.170	.8268	.1406	.2876	2.04
7	1.022	0.224	.8203	.1837	.3720	2.02
8	1.022	0.176	.8203	.1444	.2912	2.01
9	1.018	0.100	.8139	.0814	.1628	2.00
10	1.020	0.160	.8171	.1307	.2656	2.03
11	1.024	0.218	.8235	.1795	.3532	1.96
12	1.024	0.180	.8235	.1482	.3020	2.03
13	1.020	0.138	.8171	.1128	.2250	1.99
14	1.022	0.138	.8203	.1132	.2213	1.95
15	1.022	0.150	.8203	.1230	.2542	2.06
16	1.026	0.170	.8268	.1406	.2876	2.04
17	1.022	0.224	.8203	.1837	.3720	2.02
18	1.022	0.176	.8203	.1444	.2912	2.01
19	1.018	0.100	.8139	.0814	.1628	2.00
20	1.020	0.160	.8171	.1307	.2656	2.03
21	1.024	0.218	.8235	.1795	.3532	1.96
22	1.018	0.100	.8139	.0814	.1628	2.00
23	1.020	0.160	.8171	.1307	.2656	2.03

Sample No.	Diameter (cm)	Thickness (cm)	Area (cm2)	Volume (cm3)	Weight (gms)	Density (gm/cc)
24	1.024	0.218	.8235	.1795	.3532	1.96
25	1.024	0.180	.8235	.1482	.3020	2.03
26	1.020	0.138	.8171	.1128	.2250	1.99
27	1.022	0.138	.8203	.1132	.2213	1.95
28	1.022	0.150	.8203	.1230	.2542	2.06
29	1.026	0.170	.8268	.1406	.2876	2.04
30	1.022	0.224	.8203	.1837	.3720	2.02
31	1.022	0.176	.8203	.1444	.2912	2.01
32	1.018	0.100	.8139	.0814	.1628	2.00
33	1.020	0.160	.8171	.1307	.2656	2.03
34	1.022	0.138	.8203	.1132	.2213	1.95
35	1.022	0.150	.8203	.1230	.2542	2.06
36	1.026	0.170	.8268	.1406	.2876	2.04

No major effect found in the corresponding density ratios.

4.2.5 SINTERING

Sintering of the pressed pellets in a batch of 3 were carried out at different temperatures i.e. 1000°C, 1100°C & 1200°C for 3 hours in furnace.

Sintering Temp. (°C) for 3 hrs.	**Diameter (cm)**	**Thickness (cm)**	**Area (cm2)**	**Volume (cm3)**	**Weight (gms)**	**Density (gm/cc)**	**% Density**
1000	0.912	0.200	.6535	.1307	.3072	2.35	75
1000	0.912	0.160	.6535	.2633	.2633	2.51	80
1000	0.912	0.158	.6529	.1030	.2577	2.61	83
1100	0.900	0.200	.6362	.3240	.3240	2.54	81
1100	0.900	0.156	.6362	.2534	.2534	2.55	81
1100	0.900	0.130	.6362	.2134	.2134	2.55	81
1200	0.860	0.118	.5809	.1946	.1946	2.84	90
1200	0.860	0.118	.5809	.1922	.1922	2.80	89
1200	0.860	0.118	.5809	.1908	.1908	2.75	87

The density was determined by the *Archimedes Principle*.

Theoretical Density -3.156 gm/cc

- % Theoretical density = d(bulk)/d(th)*100

4.2.6 SCANNING ELECTRON MICROGRAPHS

Understanding the sintering behavior of hydroxyapatite powders is important, because this allows to design ceramics with controlled grain growth, microstructure and mech properties. In the present study, the effect of powder characteristics on densification, microstructural development and mechanical properties of HAP were studied.

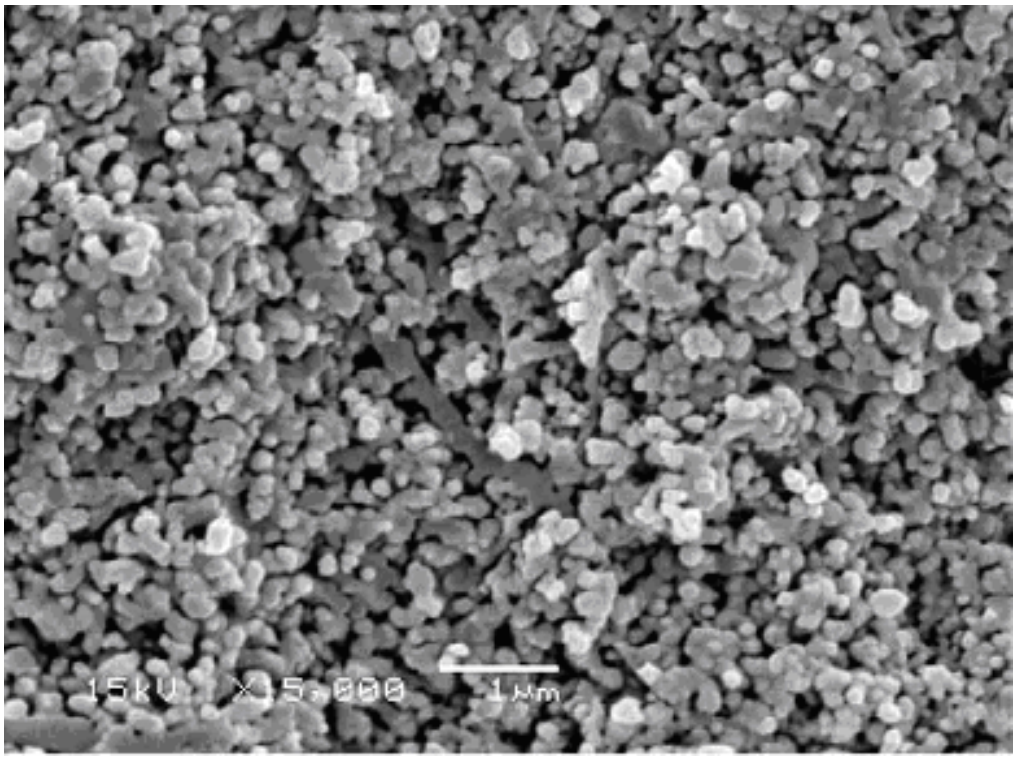


FIG.7.1SEM of hydroxyapatite sintered at 1000 ◦C:

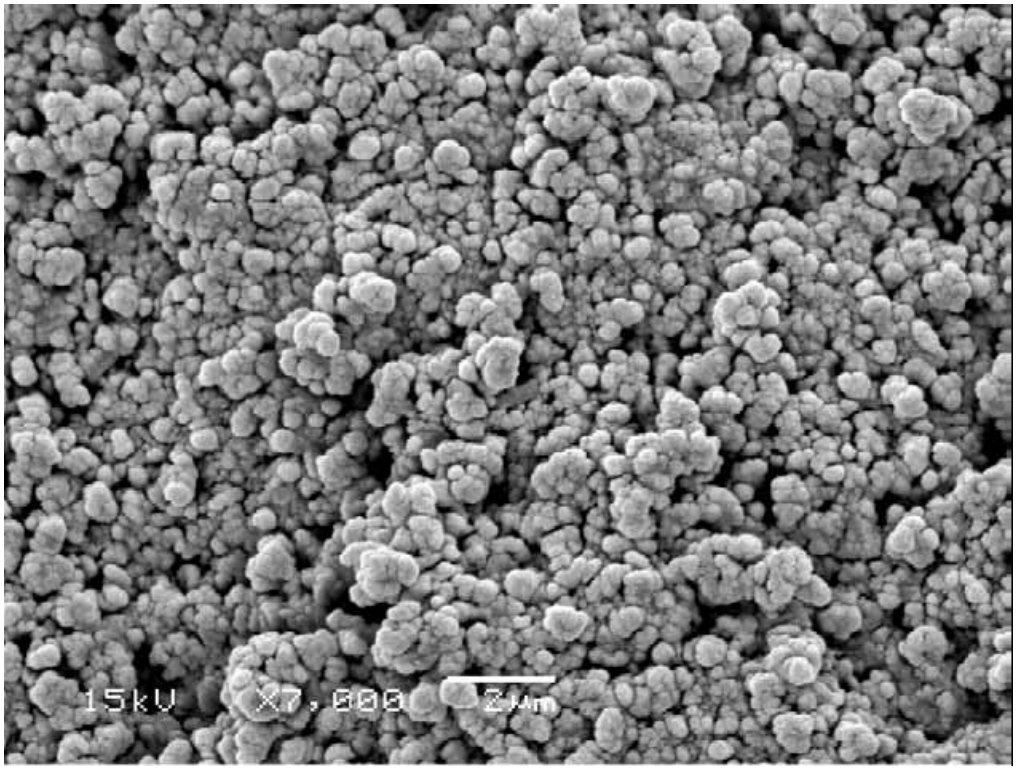


FIG.7.2 SEM of hydroxyapatite sintered at 1100 ◦C:

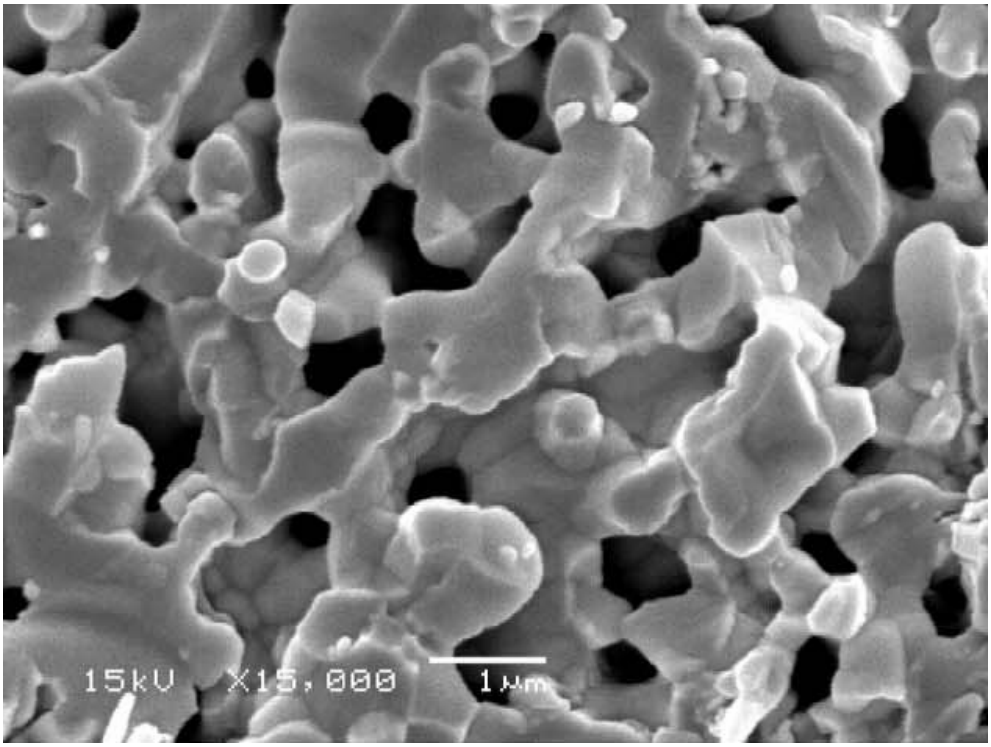


FIG.7.3 SEM of hydroxyapatite sintered at 1200 ◦C:

Chapter 5

CONCLUSIONS

HAP powder was prepared through chemical precipitation technique using $(NH_4)_2HPO_4$,$Ca(NO_3)_2$ & $Ca(NO_3)_2.4H_2O$.The present work deals with the synthesis and characterization of the powder. The significant findings of this work are:

- XRD results indicate there is an improvement in crystallinity of HAP after calcination.
- Thermal stability is there upto 1300°C and minimum weight loss
- The densification of HAP was the result of volume diffusion and grain boundary diffusion.
- There is a presence of two particle size ranges in case of HAP powders.

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